

Indirect evidence for strong coupling superconductivity in FeSe under pressure from first-principle calculations

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Whether the pairing mechanism for superconductivity in iron-based superconductors is of itinerant or local character is a question still debated on. In order to investigate the influence of Fermi surface nesting, we calculate from first-principles the static susceptibility of FeSe under applied pressures, both hydrostatic and non-hydrostatic. We show that the electronic band structures are highly sensitive to the way pressure is applied and confront our theoretical results with conclusions drawn from experiments. Given that the critical temperature of FeSe is quite universal as function of pressure, this is clear evidence that in FeSe the evolution of Fermi surface nesting cannot account for the evolution of the critical temperature with pressure. Hence we argue that the pairing in iron-chalcogenide compounds should be of strong-coupling spin fluctuation origin.

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The discovery of a new class of iron based high- T_c superconductors in 2008 [1] has kicked off an avalanche of research in solid state physics, a lot of it dedicated to the key question of the superconducting pairing mechanism. A feature that has been agreed upon is that the parent compounds of the FeAs superconductors exhibit an antiferromagnetic (AFM) spin density wave (SDW) phase, as seen in $LnOFeAs$ ($Ln = La, Ce, Pr, Sm$ [2–4]) and $AeFe_2As_2$ ($Ae = Ba, Sr, Ca$ [5–7]), or are on the verge of it, as in $AFeAs$ ($A = Li, Na$ [8, 9]). In such materials, superconductivity (SC) arises or is enhanced, respectively, when this long-range magnetic order is suppressed by doping or by application of physical or chemical pressure. In this respect, pnictide and chalcogenide compounds are much more flexible as compared to cuprate high- T_c superconductors, where the superconducting state can be reached only by doping, and intercalating layers between the copper-oxygen planes are therefore essential. This large flexibility has been underpinned by the discovery of SC in FeSe [10–13], a material lacking completely the intercalated planes of the iron-pnictides. This structural simplicity and its enormous response to external pressure (T_c increases from 8 K at ambient pressure [10] to 37 K at about 7 GPa [14]) made it a popular testing ground to study mechanisms of SC in iron-based superconductors.

Theoretical studies have shown [15–17] that iron chalcogenides are significantly stronger correlated than the iron pnictide materials. Since this goes hand-in-hand with the enhancement of localized magnetic moments, the applicability of the Fermi surface nesting (FN) scenario in this class of compounds has to be clarified. In

that scenario, SC can be regarded as a consequence of perturbations of the AFM ordering of the parent material [18–23], and suppression of peaks in the susceptibility due to FN is an indicator for the occurrence of SC.

In order to shed light on this issue we perform first-principle calculations of the static susceptibility of FeSe under pressure. Many independent experimental studies on pressure vs. T_c phase diagrams have been published for FeSe [14, 20, 24–26]. The general consensus seems to be that T_c starts around 8 K for ambient pressure, has a maximum at about 7 GPa and decreases again for higher pressures. While all the works mentioned above applied pressure hydrostatically, a recent study investigated how T_c changes under *non*-hydrostatical pressure [27]. It is interesting to observe that the corresponding phase diagram is quite similar, i.e. the way how pressure is applied seems to be of minor importance for SC.

Our results show that suppression of FN cannot be reconciled with the occurrence of SC. Furthermore, the way how pressure is applied to the system substantially changes the electronic band structure and consequently the static susceptibility. Given the universality of T_c vs. pressure, this indicates that SC in FeSe is driven by short-ranged spin fluctuations between rather localized magnetic moments [24, 28, 29].

Method: A very useful quantity for theoretical investigations of the strength and changes of the FN is the static susceptibility matrix $\chi^0(\mathbf{q})$ (in short χ^0). For a system of Bloch electrons - taking into account only the diagonal elements of this matrix - it reads in the random phase approximation

$$\chi^0(\mathbf{q}) = \frac{1}{2\pi^3} \sum_{n,m} \int_{\text{BZ}} d\mathbf{k} \frac{f_m(\mathbf{k}) [1 - f_n(\mathbf{k} + \mathbf{q} + \mathbf{G})]}{\epsilon_m(\mathbf{k}) - \epsilon_n(\mathbf{k} + \mathbf{q} + \mathbf{G})} |\langle m, \mathbf{k} | e^{-i\mathbf{q} \cdot \mathbf{r}} | n, \mathbf{k} + \mathbf{q} + \mathbf{G} \rangle|^2, \quad (1)$$

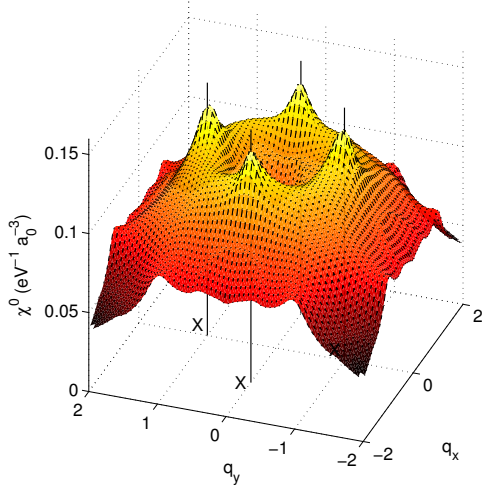


FIG. 1: Static susceptibility χ^0 in the $(q_x, q_y, 0)$ -plane of FeSe at a hydrostatic pressure of 2.8 GPa. The vertical solid black lines mark the positions of the X points in the reciprocal unit cell and q_x, q_y are given in units $2\pi/a$ and $2\pi/b$, respectively.

where \mathbf{q} represents a vector of the *extended* wave number space, n and m denote electron band indices, \mathbf{k} belongs to the first Brillouin zone (BZ), and $\epsilon_m(\mathbf{k})$ and $f_m(\mathbf{k})$ mean the energy dispersion of the m th band and the Fermi function, respectively. The reciprocal lattice vector \mathbf{G} is defined such that $\mathbf{k} + \mathbf{q} + \mathbf{G} \in \text{BZ}$. We want to stress that the matrix elements $\langle m, \mathbf{k} | e^{-i\mathbf{q}\mathbf{r}} | n, \mathbf{k} + \mathbf{q} + \mathbf{G} \rangle$ are fully included in our calculation.

FN leads to a pronounced peak of χ^0 at the nesting vector $\mathbf{q} = \mathbf{q}_N$ due to singularities of the integrand. Many undoped parent materials of iron-based superconductors show a marked FN and consequently a maximum of χ^0 at \mathbf{q}_N . A perturbation of the crystal structure due to applied pressure or of the electronic band structure due to (electron or hole) doping is able to suppress the FN and the strong response of χ^0 . It is argued [30–33] that the reduction of the collectively AFM-ordered electron spins in favor of the appearance of spin-flip processes may act as a generator for electron pairing and SC.

All results presented in this work have been obtained on the basis of non-spinpolarized DFT FPLAPW band structure calculations using the WIEN2k package [34]. The exchange-correlation potential has been approximated by the generalized gradient approximation GGA, and the base-centered orthorhombic crystal structure Cmma has been used. The numerical integration over the first Brillouin zone has been performed with a semi-analytical tetrahedron method. Each electron wave function has been represented by about 4000 plane waves, and 52 electron bands, corresponding to an energy interval from -1.2 Ry below to 3 Ry above the Fermi energy, have been included. The momentum vectors \mathbf{q} are

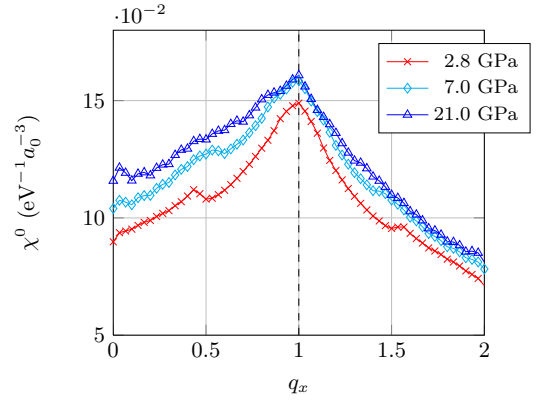


FIG. 2: Static susceptibility χ^0 in the $(q_x, 0, 0)$ direction of FeSe for different hydrostatic pressures (q_x is given in units $2\pi/a$). Apart from the vertical shift, due to the increasing density of states at the Fermi energy, χ^0 shows very little dependence on pressure.

expressed in units of $(2\pi/a, 2\pi/b, 2\pi/c)$ throughout this work, where a, b and c are the FeSe unit cell lattice parameters, and χ^0 is presented in units $(\text{eV} \cdot a_0^3)^{-1}$ with a_0 being the Bohr radius. The lattice and unit cell parameters are taken from experiment, where we used data by Margadonna *et al.* [14] and Kumar *et al.* [21] for hydrostatic pressures, and for the non-hydrostatic case data from Uhoya *et al.* [27].

Results: We start the discussion of the pressure dependence with the hydrostatic case. We checked that the results based on the crystal structures reported by Kumar *et al.* [21] are essentially the same compared to the results based on structures reported by Margadonna *et al.* [14]. In the following, we will hence show only results based on data by Kumar *et al.*. In Fig. 1 a surface plot of the static susceptibility over the $(q_x, q_y, 0)$ -plane for FeSe at a hydrostatic pressure of 2.8 GPa is presented. The dominating features are the marked peaks, indicating a strong FN of the hole pockets at the Γ point and the electron pockets at the X points, corresponding to the FN vector $\mathbf{q}_N = (1, 0, 0)$. For a better quantitative discussion of the pressure dependence, we show a $(q_x, 0, 0)$ cut of the susceptibility in Fig. 2. In this diagram we compare the susceptibility in the $(1, 0, 0)$ direction for three structures at pressures 2.8 GPa (red, \times), 7 GPa (cyan, \diamond) and 21 GPa (blue, \triangle). Interestingly, the three calculated profiles have a quite similar shape. They differ only by a vertical shift, reflecting the increase of the electronic density of states $N(\epsilon)$ at the Fermi energy ϵ_F with increasing pressure, according to the relation $\chi^0(0) = N(\epsilon_F)/\Omega_0$ where Ω_0 denotes the volume of the unit cell of the crystal. However, the prominent peak at $\mathbf{q}_N = (1, 0, 0)$ does not vanish with increasing pressure, leading to the conclusion that the strength of the FN is not pressure-dependent in the hydrostatic case.

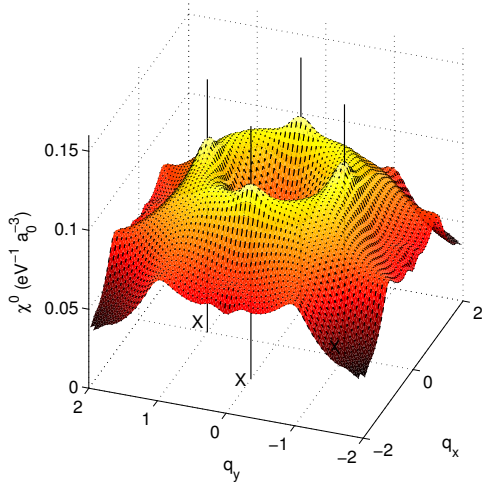


FIG. 3: Static susceptibility χ^0 in the $(q_x, q_y, 0)$ -plane for FeSe at a non-hydrostatic pressure of 4 GPa. The vertical solid black lines mark the positions of the X points in the reciprocal unit cell and q_x , q_y are given in units $2\pi/a$ and $2\pi/b$, respectively.

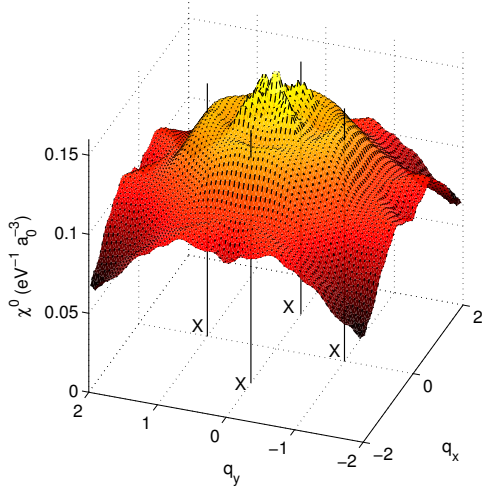


FIG. 4: Static susceptibility χ^0 in the $(q_x, q_y, 0)$ -plane for FeSe at a non-hydrostatic pressure of 12.9 GPa. The vertical solid black lines mark the positions of the X points in the reciprocal unit cell and q_x , q_y are given in units $2\pi/a$ and $2\pi/b$, respectively.

The situation is different in the non-hydrostatic case, as demonstrated in Figs. 3 and 4. Here we present the static susceptibility for the compounds reported by Uhoya *et al.* [27]. Fig. 3 depicts the situation for 4 GPa, where the marked maxima at the X points, similar to the hydrostatic case, can still be observed. On the other

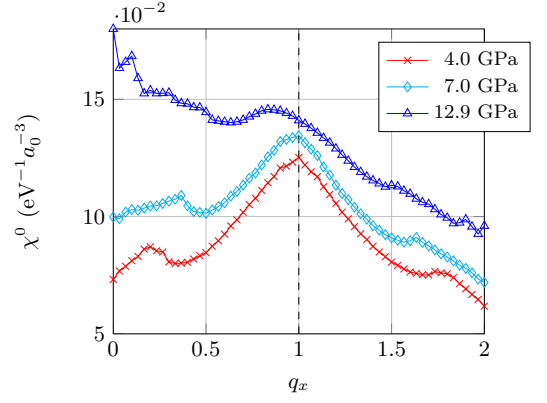


FIG. 5: Static susceptibility χ^0 in the $(q_x, 0, 0)$ direction for FeSe for different non-hydrostatic pressures (q_x is given in units $2\pi/a$). χ^0 shows a marked peak at the FN vector \mathbf{q}_N for the 4 GPa case, which is still present, albeit reduced, for the 7 GPa compound. At high pressures of 12.9 GPa no prominent feature can be seen.

hand, for the high pressure case (12.9 GPa) shown in Fig. 4, these maxima are reduced significantly. This change of the susceptibility is even better demonstrated in Fig. 5, where we depict again a $(q_x, 0, 0)$ cut of the susceptibility. Here we compare χ^0 for the case of non-hydrostatic pressures at 4 GPa (red, \times), 7 GPa (cyan, \diamond) and 12.9 GPa (blue, \triangle). For the intermediate pressure regime of 7 GPa we interpolated the structural data from Uhoya *et al.* [27] for 4 GPa and 12.9 GPa. It is known from experiments [14, 21, 35] that - in such moderate pressure regimes - the unit cell parameters change linearly with pressure, supporting this approach. While the strong response at \mathbf{q}_N is still present for the cases with 4 and 7 GPa (albeit slightly reduced for the 7 GPa structure), it has vanished completely for the high pressure case. This behavior of χ^0 allows the conclusion that the FN in FeSe is rather strong for low and reduced considerably for higher non-hydrostatic pressures.

In order to get better insight into this different FN behavior, we present in Figs. 6 and 7 the cuts of the Fermi surfaces in the $(q_x, q_y, 0)$ -plane for low (4 GPa) and high (12.9 GPa) non-hydrostatic pressures. The different colors in these diagrams correspond to different bands, while the black dotted lines mark the edges of the unit cell in reciprocal space.

For low pressures (Fig. 6), it can clearly be seen that there is a marked FN, originating mainly from the interband transitions between the hole-like pockets around the Γ point and the electron-like pockets around the X point. Different to doping, where hole pockets shrink and electron pockets grow - or vice versa - the effect of non-hydrostatic pressures is a bit more subtle: Large pressures lead to considerable changes in the a/b lattice parameters, and as a consequence, not only the sizes of

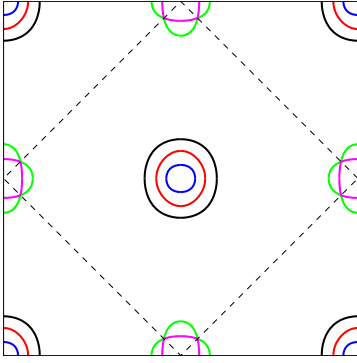


FIG. 6: Fermi surface $q_z = 0$ cut for FeSe at a non-hydrostatic pressure of 4 GPa. The different colors correspond to different electron bands that cross the Fermi energy and the black dashed lines mark the boundaries of the reciprocal unit cell.

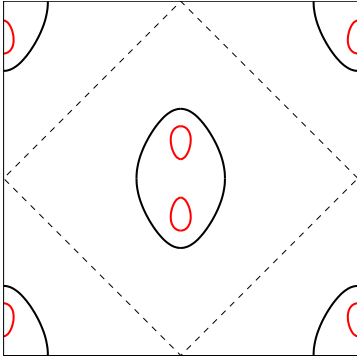


FIG. 7: Fermi surface $q_z = 0$ cut for FeSe at a non-hydrostatic pressure of 12.9 GPa. The different colors correspond to different electron bands that cross the Fermi energy and the black dashed lines mark the boundaries of the reciprocal unit cell.

the pockets, but also their shapes are altered substantially (Fig. 7). In the case of low pressures the electron and hole pockets are in good approximation circularly shaped. For high pressures on the other hand, the pockets at the X points disappear completely and the Fermi surfaces at the Γ point are distorted to more complicated elliptical shapes. This results in a complete loss of the FN vector \mathbf{q}_N and further supports our conclusion drawn from Figs. 3-5, namely, that an increasing non-hydrostatic pressure causes a significant decrease of the FN: While in the 4 GPa case the nesting vector $\mathbf{q}_N = (1, 0, 0)$ can clearly be observed, such a feature is not visible for a pressure of 12.9 GPa. We want to stress that the calculation of the complete susceptibility offers

more detailed and reliable information about the position of the SDW-vector and the strength of the FN. This is based on the fact that χ^0 involves the integration over the whole Brillouin zone and the inclusion of the matrix elements, as can be seen in Eq. 1.

Summary: The results presented above have important implications concerning the behavior of SC in FeSe. While for low pressures the static susceptibility of this material exhibits a marked FN, the higher pressure properties depend crucially on whether pressure is applied hydrostatically or not. According to our calculations there is no visible reduction of the FN for applied hydrostatic pressures, even as large as 21 GPa. On the other hand, we observe that the FN is reduced significantly if pressure is applied non-hydrostatically. Based on these theoretical results alone one might argue that - in the framework of FN-mediated pairing - SC in FeSe is only supported efficiently by non-hydrostatic pressures. However, such a result contrasts sharply with experiments, which report a considerable increase of T_c with increasing pressure *independent* of the way pressure is applied.

This leads to the conclusion, that SC in the FeSe compounds is not based on a weak-coupling nesting between electron and hole pockets, and therefore not mediated by spin fluctuations coming from an itinerant SDW state. Moreover, recent studies have shown [36–38] that the pronounced increase of T_c with pressure cannot be explained by phononic Cooper-pairing, too. Therefore, staying in the paradigm of spin-mediated pairing, we would argue that the SC in FeSe is based on fluctuations between *more localized* magnetic moments.

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